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Viscoelasticity and Birefringence of Polymer Blends

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The birefringence in the process of stress relaxation was investigated for solutions of mixtures of polystyrene (PS) and poly(vinyl methyl ether) (PVME) in dibutyl phthalate. Molecular weight (M_w) of PVME was 6.5×10^4 , and M_w of the PS samples were 2.0×10^5 , 6.0×10^5 , and 9.5×10^5 . The concentrations of PS and PVME were, respectively, 0.30 g cm^{-3} . The birefringence, Δn , and the shear stress, σ , were measured after an instantaneous shear deformation. Under assumptions that the Δn and γ are sums of independent contributions from PS and PVME chains, and that the stress-optical law holds good for the contribution from each chain, the shear stresses, σ_{PS} and σ_{PVME} , attributable to the PS and PVME chains, respectively, were separately evaluated. It was found that at long times σ_{PVME} had relaxed and the stress was supported solely by PS-PS entanglements, in accord with the previous results of viscoelasticity measurement. The stress supported by the PVME chains, σ_{PVME} , was not affected by varying molecular weights of PS.

KEY WORDS: Stress relaxation/Birefringence/Polymer blends/Entanglement/Stress-optical rule

INTRODUCTION

The viscoelastic properties of polymeric materials depend largely on the molecular weight distribution.¹⁾ The effect of the molecular weight distribution has widely been studied on the blends of two samples of the same polymer species with narrow molecular weight distributions.²⁻¹⁷⁾ We denote the molecular weights of the components as M_L and M_S , where the suffixes L and S stand for long and short polymer chains, respectively; hence $M_L > M_S$. If both of M_L and M_S are larger than the entanglement molecular weight, M_e , the relaxation modulus exhibits two plateau regions. The plateau modulus of the first plateau region (I) at shorter times is higher than the second plateau region (II) located at longer times. The modulus in region I is proportional to the number of entanglements per unit volume. At the long time end of the plateau region I, the entanglements related to the short (S) chains become ineffective as the S chains leave the effective entanglement network through the diffusion process. The plateau modulus at longer times (II) is proportional to the number of entanglements between the long (L) chains and is originated exclusively by the L chains. The relaxation of the first plateau modulus should be more complicated than that of the second; the former is not only the relaxation of stress supported by the S chains but involves the partial relaxation of the stress supported by the L chains due to the diffusion of the S chains. This conjecture is in accord with the observed results on viscoelasticity. On the other hand, it is difficult to directly confirm these facts because the separate evaluation of the contributions to stress of the respective components is not possible.

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The viscoelastic properties of the blend of unlike polymers may be similar to that of the homo-blend, if the component polymers are miscible and the interaction between unlike segments is similar to that between like segments. In such a system, we can separately evaluate the average orientation of segments of each component from the birefringence or the infrared dichroism in stress relaxation process. Saito *et al.*¹⁸⁾ studied the birefringence and infrared dichroism of the blend of poly (methyl methacrylate) and poly (vinylidene fluoride), and found that the relaxation times of the orientation of two polymers are the same and concluded that two polymers move cooperatively. Monnerie *et al.*^{19-21b)} studied blends of polystyrene (PS) with poly(phenylene oxide) or poly (vinyl methyl ether) (PVME) by flow birefringence in the elongation flow. The orientation of component polymers decayed at different rates. Kornfield *et al.*²²⁾ studied the infrared dichroism of the blend of long PS chains and short deuterated PS chains and observed that the relaxation rate of short chains is affected by the molecular weight of long chains. The present authors have studied²³⁾ the birefringence of the solutions of blend of PS and PVME and observed that the stress at long times is supported solely by the long PS chains. In the following, we investigate the birefringence accompanied with the stress relaxation process of the solutions of mixtures of PS and PVME in more details.

PRINCIPLE

The stress-optical law applicable to polymeric liquids reads

$$\Delta n = C\sigma. \quad (1)$$

where Δn and σ are the anisotropic parts of refractive index and stress tensor, respectively. The quantity, C , is the stress-optical coefficient. The relation can be derived from molecular models^{24,25)} under an assumption that the stress and the polarizability are simple sums of the contributions from all the polymer segments in the system. The assumption is believed to be valid for rubbers, melts, and concentrated solutions but not for dilute solutions, in which the distribution of segments are not so uniform as in other systems.²⁶⁾ The difference of the refractive index between the non-spherical region of the polymer coil and the surrounding liquid gives rise to the form birefringence.

The same assumption of the simple additivity may be applied to the concentrated solution containing different segment species, A and B, if the segments of each species are distributed uniformly, to the degree comparable to the distribution in the concentrated solution of one polymer species. One can hope that this condition may be realized for copolymers²⁷⁻²⁹⁾ or blends composed of miscible components. Then one obtains

$$\sigma = \sigma_A + \sigma_B \quad (2)$$

$$\Delta = C_A \sigma_A + C_B \sigma_B \quad (3)$$

where σ_A and σ_B are the anisotropic parts of the stress tensors due to the components

A and B, respectively. The coefficients, C_A and C_B , representing the optical anisotropies of respective segments, are expected to be close to the stress-optical coefficients of the polymers A and B, respectively. The quantities σ_A and σ_B may be evaluated from the experimental data of σ and Δn .

The simple shear deformation may be described with a displacement vector with respect to a Cartesian coordinate system $x_1 x_2 x_3$ as

$$u_1 = \gamma x_2 \quad u_2 = u_3 = 0 \quad (t > 0) \quad (4)$$

where γ is the magnitude of shear. The stress tensor, σ_{ij} , is determined by four components, σ_{11} , σ_{22} , σ_{33} and $\sigma_{12} = \sigma_{21}$; $\sigma_{13} = \sigma_{31} = \sigma_{32} = \sigma_{23} = 0$. We use the short hand notations

$$\sigma = \sigma_{12}, \quad N_1 = \sigma_{11} - \sigma_{22}, \quad N_2 = \sigma_{22} - \sigma_{33} \quad (5)$$

where σ is the shear stress and N_1 and N_2 are the first and second normal stress differences, respectively. These are functions of time t and γ .

In most of the studies of birefringence in shear²⁵⁾, the light is led along the neutral x_3 axis. The stress-optical law is written as

$$\Delta n_{12} \sin 2\chi = 2C\sigma. \quad (6)$$

$$\Delta n_{12} \cos 2\chi = CN_1 \quad (7)$$

where Δn_{12} is the magnitude of birefringence in the $x_1 x_2$ plane and χ is the extinction angle. When the light is led along the x_2 axis²⁵⁾, the birefringence measured is related to the stress through

$$\Delta n_{13} = C(N_1 + N_2) \quad (8)$$

Since the x_1 axis is not a principal axis, the quantity Δn_{13} is not a difference of the principal values of the refractive index ellipsoid. In the following, we study only Δn_{13} and so we write

$$\Delta n = \Delta n_{13} \quad (9)$$

In the process of stress relaxation following a stepwise shear deformation, the first normal stress difference, N_1 , is derived from the shear stress, σ , through the Lodge-Meissner relation³⁰⁾

$$N_1(t, \gamma) = \gamma \sigma(t, \gamma) \quad (10)$$

Since the second normal stress difference, N_2 , is much smaller than the first, N_1 , one obtains from eq 8 and 10 an approximate relation

$$\Delta n = C' \gamma \sigma. \quad (11)$$

or in terms of the relaxation modulus, $G(t, \gamma)$,

$$\frac{\Delta n}{\gamma^2} = C' G \quad (12)$$

Here C' is a material constant slightly smaller than the stress-optical coefficient, C . Eq 12 holds valid for PS solutions^{31,32)} and for PVME solutions as will be shown later.

One may derive corresponding equations for the polymer blend from eq 2 and 3.

$$G = G_A + G_B \quad (13)$$

$$\frac{\Delta n}{\gamma^2} = C'_A G_A + C'_B G_B \quad (14)$$

Here $G_A(t, \gamma)$ and $G_B(t, \gamma)$ are the contributions from the A and B segments, respectively, to the relaxation modulus. They might be separately evaluated from the data of G and Δn provided that C'_A/C'_B is not too close to unity. In addition to the assumption of simple additivity, the assumption of the Lodge-Meissner relation is necessary to derive the relation for the blend. The Lodge-Meissner relation is a relation for the stress following an instantaneous shear deformation. It is equivalent to the statement that the principal axis of stress are determined solely by the magnitude of shear γ or that the stress state is not affected by the deformation history within the infinitesimal period. These statements seem to be valid also for in homogeneous blends. Here we assume the validity. For confirming the relation, we have to measure σ and N_1 in the stress relaxation process. The optical version of the Lodge-Meissner relation reads

$$2\cot 2\chi = \gamma. \quad (15)$$

Measurements are in progress to prove this relation for polymer blends.

EXPERIMENTAL SECTION

Materials

Poly (vinyl methyl ether) used in this study was purchased from Scientific Polymer Products, Inc. in the form of a aqueous solution. The solution separated into two phases at high temperatures, and water could be removed at about 80°C. This polymer was dissolved in benzene and precipitated in hexane. The molecular weight was measured by combining gel permeation chromatography with light scattering ($M_w = 6.0 \times 10^4$ and $M_w/M_n = 1.3$). Three polystyrene samples with narrow molecular weight distributions supplied from Tohso, Co., and Pressure Chemical, Inc., were used without further purification. Characteristics of polymers are summarized in Table 1. Reagent-grade dibutyl phthalate (DBP; Nakaraites Co.) was distilled under reduced pressure.

The solution was prepared with the following procedure. Weighed amounts of PS, PVME, and DBP were dissolved in a sufficient amount of benzene. Benzene was subsequently evaporated very slowly from solution. The test solution for measurement was clear to the naked eye at the room temperature.

Table 1 Characterization of polymer samples.

code	$M_w/10^4$	M_w/M_n
PS20	19	1.04
PS60	59	1.06
PS90	95	1.10
PVME	6.0	1.3

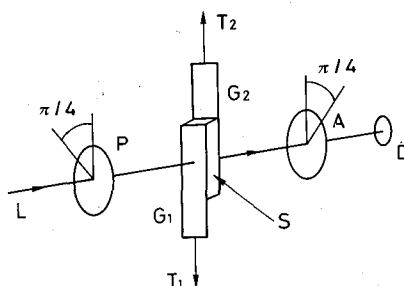


Fig. 1 Alignment for the optical measurement.

Experimental method

The details of the instrument for the measurements of birefringence in the stress relaxation process were reported previously³³⁾. Here the principle of measurement is described roughly in Figure 1. The test solution, S, is filled in a gap between a pair of parallel glass plates, G_1 and G_2 . The shear deformation is applied to the solution through parallel motion, T_1 and T_2 , of the plates. The shear stress is evaluated from the force applied to the plates. Two polarizing films, P and A, are placed in parallel with the glass plates. The polarization directions of P and A are set equal to $\pi/4$ and $-\pi/4$, respectively, with respect to the direction of shear. By measuring the intensity of light beam that passed through P, test solution, and A, one can evaluate the birefringence, Δn , the difference between the refractive index in the shear direction and that in the neutral direction. Measurements were performed at various magnitudes of shear, γ , ranging from 0.7 to 1.1. The quantities σ/γ and $\Delta n/\gamma^2$ were independent of γ over this range.

For obtaining the relaxation modulus at short times, the dynamic complex modulus was measured with a cone-and-plate type rheometer (Rheopexy Analyzer, Iwamoto Seisakusho Co., Kyoto). The magnitude of shear was 0.8 and the range of the angular frequency was $6.28 \times 10^{-2} < \omega/s^{-1} < 6.28$. The complex modulus was converted to the relaxation modulus with an approximation formula of Nimoniya and Ferry³⁴⁾.

RESULTS AND DISCUSSION

Birefringence of PS and PVME solutions

The birefringence and relaxation modulus of solutions of PS90 in DBP and PVME in DBP after instantaneous shear deformation at 20°C are shown in Figure 2. The

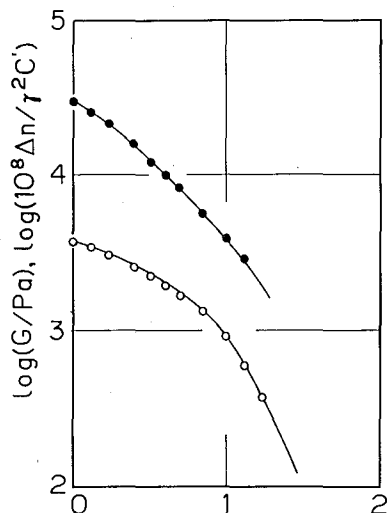


Fig. 2 Quantity $C'^{-1}\gamma^{-2}\Delta n$ for 0.3 gcm⁻³ solution of PS(unfilled circles; $M_w=9.5\times 10^5$) and 0.9 gcm⁻³ solution of PVME(filled circles) in DBP at 20°C. Solid lines represent relaxation modulus $G(t)$.

concentration of the PS solution is $c_{ps}=0.30$ gcm⁻³, and that of the PVME solution is $c_{PVME}=0.90$ gcm⁻³. Two curves represent $G(t)$ of PS and PVME, respectively, from the top. The time range of these data corresponds to the terminal flow region.

The filled and unfilled circles represent the results for birefringence measurements for PS90 and PVME solutions, respectively, expressed as the ratios, $\Delta n/\gamma^2 C'_{ps}$ and $\Delta n/\gamma^2 C'_{PVME}$, respectively. Here, the values of C'_{ps} and C'_{PVME} were chosen to attain the best fit of the above-mentioned ratios to $G(t)$ data. One sees that the fit is very good over the whole range for both of the polymers: eq 12 holds very well. The estimated values of C'_{ps} and C'_{PVME} are -3.6×10^{-10} Pa⁻¹ and 6.3×10^{-11} Pa⁻¹, respectively. The difference between C'_{PVME} and C'_{ps} may be large enough for evaluation of contributions to stress from component polymers with eq 13 and 14.

Birefringence of blends

For the PS/PVME-DBP solutions, the simple proportionality between $\Delta n(t)$ and $\sigma(t)$ will not hold well. This is because two components of stress, σ_{ps} and σ_{PVME} , may decay at different rates. However, one expects to observe the proportionality at long times where the stress is supported by PS chains and σ_{PVME} is zero provided that $M_{ps}\gg M_{PVME}$. In this case, one may further expect that the proportionality coefficient may be close to C'_{ps} .

The values of $G(t)$ and $\Delta n/\gamma^2 C'_{ps}$ for the solutions of the mixture of PS and PVME are shown in Figure 3 with dashed and solid lines, respectively. Here, the value of C'_{ps} in the PS-DBP solution was employed for calculating the ratio $\Delta n/\gamma^2 C'_{ps}$. The concentrations of the polymers were $c_{ps}=c_{PVME}=0.30$ gcm⁻³. Measurements were done at 5°C. Judging from the shape of the curves for $G(t)$ and the magnitudes of $G(t)$, one sees that the time range of Figure 3 corresponds to the long time range of relaxation including the plateau region II (for the upper two curves), and the terminal flow region discussed in the introduction section (for all the curves). The quantity $\Delta n/\gamma^2 C'_{ps}$ is approximately equal to $G(t)$ at long times. At very short times, the former is lower

than the latter. In this time region, the stress due to PVME chains may remain unrelaxed. This is expected to reduce the birefringence because C'_{PVME} and C'_{PS} have different signs.

It has been found that the stress-optical coefficient slightly varies with varying solvent.²⁵⁾ The agreement of $G(t)$ with $\Delta n/\gamma^2 C'_{PS}$ at long times may indicate that C'_{PS} remains unchanged on mixing with PVME. If this is true, the observed behavior at long times is in accord with that of the homo-blend discussed in the introduction section. Here, we assume that C'_{PS} as well as C'_{PVME} does not vary in the mixed solution. In the following discussion, we use the value of C'_{PVME} in the PVME-DBP solution for C'_{PVME} in the PS/PVME-DBP solution without the experimental check. The assumption will be examined in the future with a solution in which $M_{PVME} > M_{PS}$.

Contributions from Component Polymers

The contributions to the relaxation modulus from the PS and PVME chains, G_{PS} and G_{PVME} , respectively, were evaluated from the data of Figure 3 with eqs 13 and 14, and shown in Figure 4. The coefficients C'_{PS} and C'_{PVME} were assumed to be equal to those of the solutions of respective polymers in DBP. The unfilled circles represent G_{PS} and filled circles G_{PVME} in Figure 4. The thick lines represent relaxation moduli of the blend solutions, $G = G_{PS} + G_{PVME}$. Obviously, G_{PS} is much larger than G_{PVME} in this time range and G_{PVME} becomes a negligibly small portion of G at times longer than 30 s.

It may be noted that G_{PVME} is approximately independent of the molecular weight of PS in the mixture. The G_{PVME} for the solution with $M_{PS} = 1.9 \times 10^5$ is slightly higher

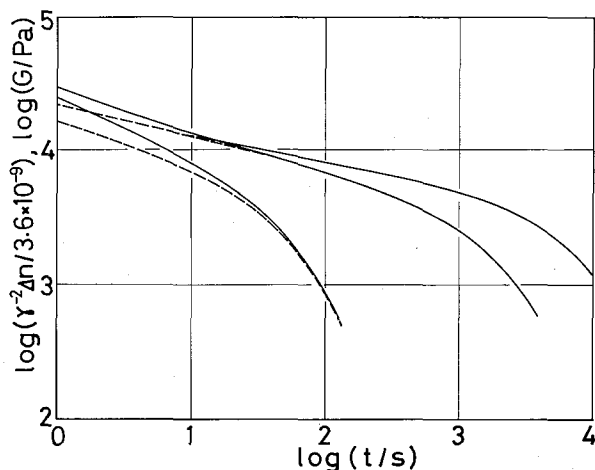


Fig. 3 G (Solid lines) and $\Delta n/\gamma^2 C'_{PS}$ (dashed lines) for solutions containing 0.3 gcm^{-3} of PS and 0.3 gcm^{-3} of PVME at 5°C . Molecular weights of PS are 9.5×10^5 , 5.9×10^5 , and 1.9×10^5 from top to bottom.

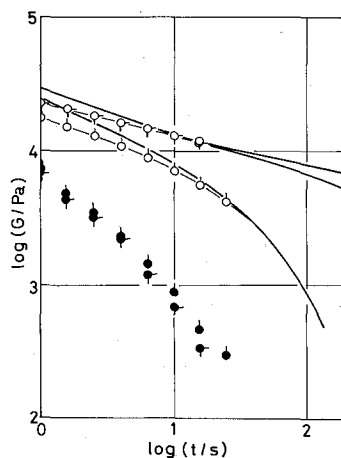


Fig. 4 G_{PS} (unfilled circle) and G_{PVME} (filled circle) evaluated from the data of Figure 3. Molecular weights of PS are 1.9×10^5 (pip up), 5.9×10^5 (pip right), and 9.5×10^5 (pip down). Thick curves represent $G = G_{PS} + G_{PVME}$.

than for other solutions but the difference is just on the verge of the uncertainty of the data; G_{PVME} is the difference of two big numbers in this range. The result indicates that the relaxation of orientation of PVME segments is not affected by the variation of the rate of relaxation of G_{PS} in this series of mixtures. This result is in contrast with that observed for the mixture of PS of different molecular weights²²⁾, for which the relaxation of short chains was retarded by raising the molecular weight of long chains. The nematic interaction proposed then³⁵⁾ does not exist in the present mixture of PVME, and DBP.

Properties of G_{PS} for High M_{PS}

The quantity G_{PS} is expected to include the effect of entanglement between PS and PVME chains as well as that between PS and PS chains. Thus, it should be larger than G^0_{PS} , the relaxation modulus of the solution of the same PS in an ordinary solvent which exerts the same friction of PS segments as the mixture of DBP and PVME does. We assume that the quantity G^0_{PS} is equal to the relaxation modulus of the solution of the PS in DBP if the unit of time is adequately chosen so that the maximum relaxation time of the assumed G^0_{PS} agrees with that of G_{PS} . The relaxation modulus of the PS-DBP system is plotted in double-logarithmic scales and shifted along the abscissa until the data overlap with those of G_{PS} at long times.

The results for the case of $M_{PS}=9.5 \times 10^5$ and $c_{PS}=0.30$ gcm⁻³ is shown in Figure 5. The dashed line represents the G^0_{PS} obtained through above-mentioned procedure. This agrees with G_{PS} (unfilled circles and solid line) at times longer than 25 s. Thus the quantities G , G_{PS} , and G^0_{PS} agree with each other over quite a wide range of time. Squares represent the quantity ΔG_{PS} and filled circles represent G_{PVME} taken from Figure 4. Here ΔG_{PS} is defined by

$$\Delta G_{PS} = G_{PS} - G^0_{PS} \quad (16)$$

and is a measure of the increase of the contribution of PS chains due to the interaction with the PVME chains. The result for the case of $M_{PS}=5.9 \times 10^5$ is the same as Figure

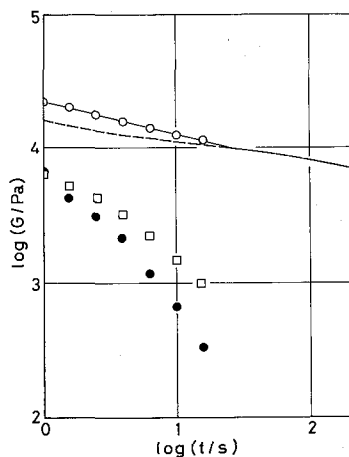


Fig. 5 G_{PS} (unfilled circle), G^0_{PS} (dashed line), $G_{PS} - G^0_{PS}$ (squares), and G_{PVME} (filled circle) for the case of $M_{PS}=9.5 \times 10^5$.

5 at times shorter than 20 s, to which the following discussion is limited.

The quantity ΔG_{PS} is higher than G_{PVME} except at the shortest times examined and the difference is not due to the uncertainty of the data. It should be remarked that the quantity ΔG_{PS} for the case of $M_{PS}=5.9 \times 10^5$ and 9.5×10^5 is not affected by the difference of M_{PS} . Many of the reports on the binary blend of the same species of polymers^{10,11,16)} state that the relaxation time of the quantity corresponding to ΔG_{PS} increases with the molecular weight of the longer chain; e.g., it is proportional to M_L^2 . The definition of the quantity corresponding to ΔG_{PS} varies slightly in various reports and is not exactly identical to the present definition. Still the difference for the cases of $M_{PS}=5.9 \times 10^5$ and 9.5×10^5 would be quite large if the relaxation time varies in proportional to M_{PS}^2 ; $(9.5 \times 10^5 / 5.9 \times 10^5)^2 = 2.5$. The difference should well be detected even if the definition of ΔG_{PS} is slightly different from what the previous authors implied. Thus the present observation that ΔG_{PS} is independent of M_{PS} seems to be in conflict with some published results.

Properties of G_{PS} for Low M_{PS}

The case of $M_{PS}=1.9 \times 10^5$ is slightly different from above. The dashed line in Figure 6 represents the G_{PS}^0 produced by shifting the relaxation modulus for the 0.30 gcm⁻³ solution of PS with $M = 1.9 \times 10^5$ on log-log graph. The shift factor was chosen so that the resulting G_{PS}^0 agrees G_{PS} at the longest time of measurements. In contrast with Figure 5, G_{PS}^0 is considerable lower than G_{PS} over almost whole range of time. Accordingly ΔG_{PS} is much higher than G_{PVME} . In fact, ΔG_{PS} is higher than that for higher M_{PS} of Figure 5. This difference may imply that the dashed line derived from the relaxation modulus of the PS solution can not be naively interpreted as G_{PS}^0 when M_{PS} is relatively low. Actually, one obtains a curve (thick line) to almost reproduce G_{PS} by plotting twice of the relaxation modulus of the 0.3 gcm⁻³ solution of PS in an appropriately reduced time scale.

On the other hand, one notes that the quantity ΔG_{PS} is quite close to the dashed line over a certain range of short times. This may indicate that a half of the stress supported by the PS chains in this time range is due to the PS-PS entanglement and

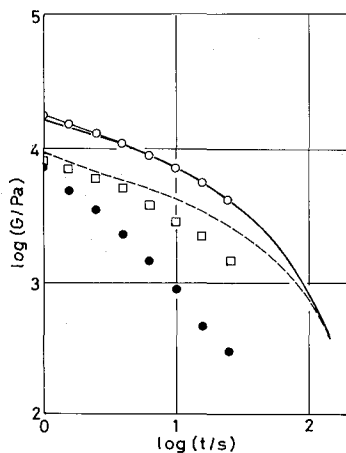


Fig. 6 G_{PS} (unfilled circle), G_{PS}^0 (dashed line), $G_{PS} - G_{PS}^0$ (squares), and G_{PVME} (filled circle) for the case of $M_{PS}=1.9 \times 10^5$. Thick line represents $2G_{PS}^0$ with reduced abscissa as described in text.

another half to the PS-PVME entanglement. This conjecture is possible because $c_{PS} = c_{PVME}$ in the present case. It can be easily tested by experiments with different concentrations of PS and PVME in the blend.

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